LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

An Extension of the Analytic Method of Analysis of Electron Diffraction Photographs of Gases

In the analysis of electron diffraction photographs of gases, a generally accepted procedure[1] is to plot I *versus* x, of the function

$$I=\sum_{ij} Z_iZ_j \frac{\sin l_{ij}x}{l_{ij}x}, \tag{1}$$

for various values of the parameters l_{ij}, and to choose those values for which the corresponding curve shows the best fit with the experimentally determined intensity distribution both in general shape and in the positions of the maxima and minima. When the molecules under investigation are large and do not possess many elements of symmetry, the computations which are necessary to determine how small changes in the parameters will affect the theoretical curves become excessive since such effects cannot be calculated directly; a new curve must be obtained for every variation. An extension of the analytic method[2] is given below, which enables one to compute the trends of the changes in the curves as the parameters are given various increments.

Suppose a plot of the above function is available for a set of the parameters. The values of $x(x_m)$ at which I reaches an extremum are therefore known. Analytically, these are given by the equation

$$S=\frac{\partial I}{\partial x}=0=\sum_{ij} Z_iZ_j \frac{1}{x}\left(\cos l_{ij}x - \frac{\sin l_{ij}x}{l_{ij}x}\right)$$

so that

$$\sum_{ij} Z_iZ_j \left(\cos l_{ij}x_m-\frac{\sin l_{ij}x_m}{l_{ij}x_m}\right)=0 \tag{2}$$

is satisfied for the set x_m obtained from the curve. Suppose now that small changes in the parameters l_{ij} are made and it is desirable to find the corresponding changes in the positions of the maxima and minima. If the new parameters $p_{ij}(=l_{ij}+\Delta l_{ij})$ are substituted in (2), the equation takes the form

$$\sum_{ij} Z_iZ_j\left(\cos p_{ij}x_m-\frac{\sin p_{ij}x_m}{p_{ij}x_m}\right)=S_m \tag{3}$$

for each particular m, where S_m differs slightly from zero. A one term Taylor's expansion gives

$$(\partial S_m/\partial x_m)\Delta x_m \approx \Delta S_m \approx -S_m, \tag{4}$$

which may be solved for Δx_m when the derivative of (3) is obtained: thus,

$$\frac{\partial S_m}{\partial x_m}=-\sum_{ij} Z_iZ_j \frac{1}{x_m}\left(x_m p_{ij} \sin p_{ij}x_m+\cos p_{ij}x_m-\frac{\sin p_{ij}x_m}{p_{ij}x_m}\right).^3$$

Once the new positions of the extremal values of I are computed in terms of the new parameters, it is a simple matter to obtain the intensities at these points on the new curve through the use of the expression

$$I_m{}^1=\sum_{ij} Z_iZ_j \frac{\sin p_{ij}(x_m+\Delta x)}{p_{ij}(x_m+\Delta x)}.$$

There now arises the question of utility. Since the values of $\partial S_m/\partial x_m$ at the troughs and peaks are quite large, a small error in estimating the initial values of x_m will introduce a relatively large error in the calculation of S_m (Eq. (3)), and consequently in Δx_m. And indeed, several numerical examples demonstrate this to be the case. Although the theoretical intensity curves as they are plotted in this laboratory may be read with an accuracy which is adequate for present-day electron diffraction photographs, they are not on a sufficiently large scale to permit the use of the more sensitive procedure outlined above. Hence the purpose of this note is merely to complete the analytic method I have previously suggested. Using (3) and (4) one may calculate, in principle, the direction and magnitude of the shifts in the peaks and troughs of the scattering function and of the corresponding changes in the intensity of that function due to arbitrary variations of the parameters. The reverse problem, that is, the computing of the necessary increments in the parameters when the changes in the positions of the extremal values are given (say, as obtained from experiment), is a much more difficult one since the various x_m's are not independent so that a solution of a set of nonlinear simultaneous equations must be undertaken. A method of employing successive approximations has already been outlined.[2]

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[1] L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936).
[2] S. H. Bauer, J. Chem. Phys. 4, 406 (1936).

[3] These calculations are simple to perform once a plot of the function $(\cos z-\sin z/z)$ and of its derivative are made. Then,

$$(\partial S_m/\partial x_m)=\sum_{ij} Z_iZ_jp_{ij}\partial/\partial z(\cos z-\sin z/z),$$

where $z=p_{ij}x_m$.